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Abstract

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CHEMISTRY

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ON THE REACTION OF WHITE PHOSPHORUS WITH ALKYL HALIDES BY IONIC AND RADICAL MECHANISMS

(Presented by Academician M. M. Shemyakin on 12 V 1964)

The simplest and most elegant method for obtaining organometallic compounds is the reaction of active metals with halogen derivatives RX. White phosphorus, as is evident from its ability to displace Cu and Pb from aqueous solutions of their salts, approaches metals of this kind, and therefore it may be called a pseudometal. By donating electrons to $R—X$, phosphorus could cause the appearance of free radicals. On the other hand, in the tetrahedral molecule $:P_4$ the presence of lone electron pairs should be manifested. The "basic" properties of $:P_4$ should be expressed more strongly than in $:PCl_3$, and probably more weakly than in $:PH_3$ and $:PR_3$, since, according to B. V. Nekrasov (^{1}), the relative electronegativities of H, P, and C in typical compounds (1; 1.13; 1.19) are close; this is confirmed by the identical electronegativity values of H and P according to Pauling (2.2) and by the small dipole moment of PH_3 (0.55 D). Not only $:PH_3$, but even $:PCl_3$, is capable of adding $R—X$, more readily in the presence of $AlCl_3$, i.e., undoubtedly by the ionic type in the form $R^+AlCl_4^-$ or a form close to it (^{2}). This gave grounds to expect a comparatively easy addition to $:P_4$ of active alkylating agents RX by an ionic mechanism, which is more promising for synthetic purposes.

The radical pathway of the reaction was most probable for halogen derivatives of the type $Cl_3\overset{\downarrow}{C}—Br$. Indeed, trichlorobromomethane reacted rapidly with P_4 upon heating below the boiling point. However, the principal solidifying fraction of the reaction mass, with b.p. 90-110° at 17 mm, consisted mainly of $Cl_3C—CCl_3$, the dimerization product of the trichloromethyl radical $Cl_3C\cdot$.

The reaction by the ionic mechanism, as we suppose, predominated under the action of alkyl halides of the type $C_6H_5\overset{+\delta}{C}H_2—Br$. Thus, upon heating to 150° for

1.5 hours, 97 g of $C_6H_5CH_2Br$ with 10 g of P in a stream of CO_2, all the phosphorus entered into the reaction, with evolution of HBr being observed. After 6 hours of holding below the boiling point, the mixture was distilled in vacuum. The following fractions were isolated: I, toluene with b.p. 110° and n_D^{15} 1.499, about 5 g; II, PBr_3, with b.p. 169-172°, about 6 g; III, benzyldibromophosphine, with b.p. 142-143° at 10 mm, 27 g ($\sim$ 30% based on P)—a colorless fuming liquid.

Found, %:	P 10.8; Br 57.2.
$C_7H_7Br_2P$. Calculated, %:	P 11.0; Br 56.7.

Upon crystallization of the residue from the distillations from aqueous alcohol, about 30 g of bromide of tetrabenzylphosphonium was obtained, with m.p. 215-216° ($\sim$ 45% based on $C_6H_5CH_2Br$ and 20% based on P).

Found, %:	P 6.4; Br 16.2; C 70.1; H 5.8
$C_{28}H_{28}BrP$. Calculated, %:	P 6.5; Br 16.8; C 70.7; H 5.9

If, after carrying out the reaction, the mixture is diluted with CCl_4, filtered, and the phosphonium salt is washed with CCl_4, then by fractionation of the solution one can obtain a signi-

considerably larger amounts of benzyldibromophosphine, with some decrease in the yield of $(C_6H_5CH_2)_4PBr$. CH_3I entered completely into reaction with P in 4 h at 100°, while $C_6H_5CH_2I$ reacted many times faster. Thus, the use of active bromides and iodides of alkyls in the reaction with P makes possible the convenient and rapid preparation of a number of organophosphorus compounds. The activity of R—Cl can probably be increased by adding suitable acids ($AlCl_3$, etc.), which greatly increase the polarization

$$\mathrm{R{-}Cl} - - \to \mathrm{AlCl_3}$$

up to the formation of R^+.

The ionic mechanism of the reaction of R—X and $:P_4$ may be represented as follows:

$$\mathrm{R^+ + :P_4} \longrightarrow \mathrm{(I)} \longrightarrow \mathrm{(II)} \longrightarrow$$

$$\xrightarrow{\mathrm{RX}} \mathrm{(III)} \xrightarrow[\mathrm{-R_3P}]{\mathrm{RX}} \mathrm{(IV)}$$

$$\mathrm{IV + RX} \longrightarrow \mathrm{RPX{-}PX{-}PX_2} \xrightarrow{\mathrm{RX}} \mathrm{R_2PX + PX_2{-}PX_2} \longrightarrow$$

$$\xrightarrow{\mathrm{RX}} \mathrm{RPX_2 + PX_3}$$

The addition of R^+, free or at the moment of reaction of R—X, to the lone pair of electrons of $:P_4$ gives the cation RP_4^+ (see I). Polarization of the P—P bonds in I leads to addition of X^- and formation of RP_4X (see II). Continuation of this kind of process gives a mixture of R_3P, R_2PX, RPX_2, and PX_3 (underlined in the scheme). Upon further reaction involving RX, a more or less equilibrium mixture of these compounds and R_4PX is formed. In the described case of the reaction of P with $C_6H_5CH_2Br$, the circumstances favored the formation of $C_6H_5CH_2PBr_2$, $(C_6H_5CH_2)_4P^+Br^-$, and PBr_3. These compounds took part in the reaction, in particular $R_4P^+X^-$ as a donor of R^+ and X^-. Reacting with P_4, like Cu^{2+} and Pb^{2+}, they led to the formation of free alkyls:

$$R_3^+P{-}R + P_4 \rightarrow R_3P^+ + R\cdot + P_4^+.$$

The cations RPX_3^+ and $R_2PX_2^+$ acted on $C_6H_5CH_2X$ as halogenating agents with formation of HX. The side formation of toluene probably occurred by radical mechanisms:

$$C_6H_5CH_2\cdot + HBr \rightleftarrows C_6H_5CH_3 + Br\cdot,$$

$$C_6H_5CH_2\cdot + C_6H_5CH_2Br \rightleftarrows C_6H_5CH_3 + C_6H_5\dot{C}HBr.$$

In the interaction of $C_6H_5CH_2Cl$ with P in sealed tubes at 300°, when HCl remained in the reaction sphere and the high temperature favored radical processes, toluene became the main product (^{4}). Transformations of $C_6H_5CH_2\cdot$ and $C_6H_5\dot{C}HX$ could lead to the formation of a number of other compounds.

L. M. Smorgonskii took part in this investigation in 1951. In the cited article (^{4}), a review was given of other works on the reaction of P with halogen derivatives; its authors were also aware of the initial results of our investigation.

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* At the corners of the tetrahedron $:P_4$ and of its adducts there are atoms $:P$ with lone pairs of electrons. It is necessary, however, to take into account the

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bent, π-like character of the P—P bonds in three-membered rings. Therefore addition of R^+ in the initial phase may also proceed by the mechanism accepted for cyclopropane (^{3}). Addition of R—X, as such, may occur through use of the *d*-orbitals of phosphorus for bonding with X.

Note: Figure translations are in progress. See original paper for figures.

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